N64 13160

Technical Report No. 32-468

Rupture Behavior of Elastomers: Effect of Statistical Variability and Crosslink Density

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October, 1963

RUPTURE BEHAVIOR OF ELASTOMERS: EFFECT OF STATISTICAL VARIABILITY AND CROSSLINK DENSITY

T. L. Smith (1) has recently proposed that rupture data for elastomers be examined in terms of a failure envelope, a plot of log σ_b (T_0/T) versus log ϵ_b. σ_b is the tensile strength based on the original cross-sectional area, (T_0/T) is the usual temperature reduction factor, and ϵ_b is the rupture strain. For materials which obey time-temperature superposition, the shape of the failure envelope is independent of the test rate or temperature, although changes in these variables shift the location of response along the envelope.

We wish to report an investigation of the effects of statistical distribution of break properties on the resolution of the envelope and the effects of changing the crosslink density on its shape and location in the
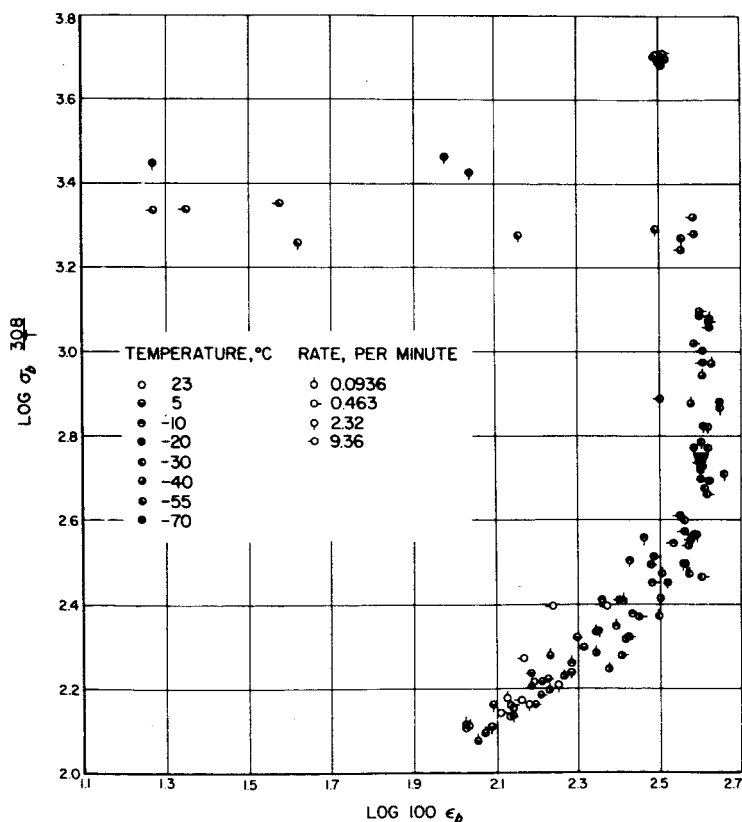

Fig. 1. Failure envelope for a peroxide cured SBR vulcanizate, M_c = 5,500 g./mole.
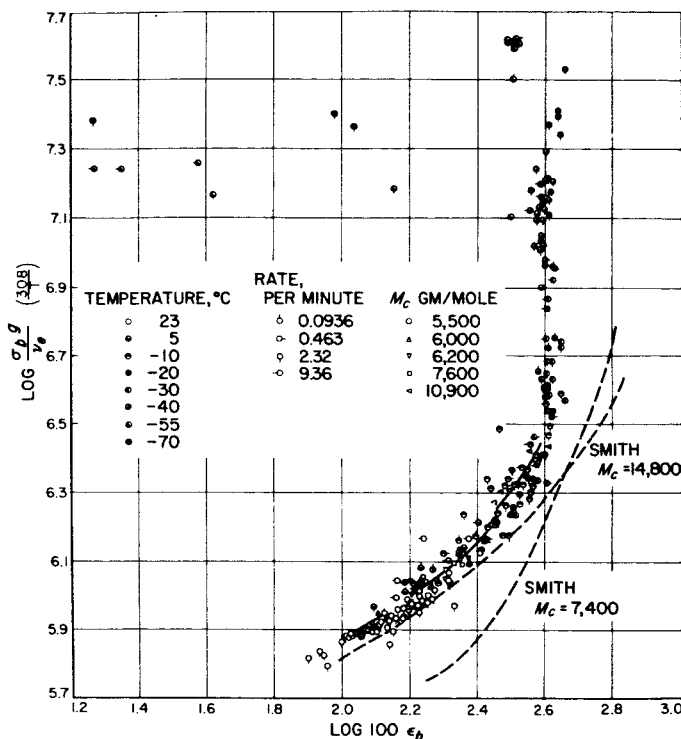
Fig. 3. Reduced failure envelope for the data shown in Figs. 1 and 2.

Figure 2 indicates the envelope of Figure 1 as the dashed line and the individual results from the larger sample populations. At high and intermediate temperatures, the statistically distributed data agree with the average curve obtained from single samples tested at varying rates and temperatures. Thus the stress-strain curves in this region either co-incide with or are parallel to the envelope, so the latter can be obtained by breaking a large number of samples at one convenient test rate and one or two temperatures. At low temperatures, when the failure strain begins to decrease, the stress-strain curves, even in the absence of cold drawing, would no longer be parallel to the failure envelope, and the dis-tribution of rupture points would cut across the envelope. Thus, in this region, several samples must be tested at any given rate or temperature in order to define the location of the envelope.

Crosslink Density. Smith (2) has noted that the high temperature end of the failure envelopes of five rubbers differed by a factor equal to the equilibrium modulus; however, the modulus variation was not very great. According to the theory of Bueche and Dudek (3), the tensile strength should vary as (ν_e/g), where g is the gel fraction and ν_e is the concen-tration of effective chains per gram of whole polymer. Accordingly, we

have tested four other samples of SBR cured to M_c's of 10,900, 7,600, 6,200, and 6,000 g./mole, the value for the first sample being 5,500, all determined by swelling in benzene at 25°C. taking $\mu = 0.34$. Three to six rings from each sheet were tested at a strain rate of 2.32/min. at 23°C., i.e., a portion of the envelope was obtained from statistical variability. These results are also shown in Figure 2. Both failure stress and strain vary with M_c, hence, a new portion of the failure envelope is being scanned, i.e., the area of response in the log σ_b, log ϵ_b plane is shifted to the right as M_c is increased. For M_c values higher than about 10,900, where there is ample evidence that at constant rate and temperature, both breaking stress and strain continue to increase with increasing M_c, one would expect the response to be shifted upward and to the right.

Employing the measured (g/ν_e) factors, the data are re-plotted in Figure 3. The data points for $M_c = 5,500$ from Figures 1 and 2 are also shown. It can be seen that the factor (g/ν_e) superposes the final four samples on the first to within the experimental error of the latter (±5%). Thus the observation of Smith and the prediction of Bueche are confirmed. Note that within certain limits, the effect on the reduced failure envelope of increasing M_c at constant rate and temperature is equivalent to increasing the rate or decreasing the temperature when M_c is held constant.

The complete failure envelopes are curves open toward the log σ_b axis. As M_c increases, the maximum value of log ϵ_b increases. As a result only the lower portions of a series of envelopes representing an increasing M_c can be superposed by use of the factor (g/ν_e). The remainder of the envelope will diverge from the common response at progressively higher values of strain. Thus the strain region at which the envelope has an infinite slope is also a measure of M_c.

As a check, on the (g/ν_e) factor, the published failure envelope data on sulfur cured SBR of Smith (1), reduced by the factor (g/ν_e) were also compared to Figure 3. We took M_c values as determined by swelling in benzene and assumed $g = 0.9$. The results for our samples and his of $M_c = 14,800$ are in good agreement, but for some reason his of $M_c = 7,400$ seem to be too low.

As a further check of the prediction, samples of polybutadiene (PBD), Firestone Diene NF 35, were cured with sulfur and mercaptobenzothiazole to M_c values of 7,700, 8,600, and 9,800. These were tested in quadruplicate at a strain rate of 2.32/min. at twelve temperatures in the range 80 to −70°C. However, when the reduced PBD failure envelope was compared with the reduced SBR envelope, it was found necessary to decrease the measured PBD M_c values by a factor of 1.4 in order to effect superposition. This discrepancy could be due to the use of an inappropriate value of μ, which we took to be 0.44 as reported by Trick (4); his samples had a different cis-trans-vinyl composition than ours so that

the use of his value of μ is questionable. A slightly smaller value of
this parameter would bring the experimental results into accord. The
high temperature stress-strain curves for the two rubbers are very near-
ly the same, which would also indicate that the M_c's calculated for PBD
using $\mu = 0.44$ are too high.

Thus, it can be concluded that the relative concentration of network
chains in samples of a given rubber type can be rapidly and convenient-
ly determined by testing multiple samples at one rate and a suitable
temperature. The vertical separation of the curves corresponds then to
the logarithm of the relative concentration of chains. If the concentra-
tion is known for one sample, the values for the other samples can be
determined absolutely. The temperature should be high enough to give
breaking strains less than about 300%. Conversely, a portion of the re-
duced failure envelope can be generated by testing multiple samples of
a polymer having varying crosslink densities at one rate and one tem-
perature.

The swelling technique has been used here to obtain the M_c values.
However, it would be anticipated that M_c values obtained from "equi-
librium" modulus measurements would also be suitable for the purpose.

The effect of M_c on strength is usually given in terms of the familiar
σ_b versus ν_e plots, which are characterized by the occurrence of a max-
imum in σ_b at low ν_e. However this maximum, which is time dependent
(3,7), is an artifact caused by the relative rates at which σ_b and ϵ_b
change with M_c. When such data are plotted as a reduced failure curve,
$\log (\sigma_b g/\nu_e)$ versus $\log \epsilon_b$, this maximum disappears. In addition, ac-
cording to the data of Bueche and Dudek, the reduced failure curve rep-
resentation of σ_b, ν_e data is time independent over the range of strain
rates covered.

The range of M_c values investigated here provides a satisfactory
check on the theory. However, it would be desirable to be able to report
reduced failure envelope data for samples having greater variations in
M_c. Work is currently in progress to obtain the data. Literature data do
not provide a suitable check on the theory since they suffer from one or
more of the following defects: (1) insufficient data available to assess
the failure envelope, (2) M_c not varied widely enough, and (3) M_c not
reported or determined. However, semiquantitative agreement with theo-
ry is provided on SBR by the data of Bueche and Dudek (3) and by Ep-
stein and Smith (5) and on an epoxy resin well above T_g by the data of
Kaelble (6).

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